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Structure of Alkali Lignins Fractionated from Ricinus communis and Bagasse.
1. Chemical Constituents

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ABSTRACT

Fractionation of alkali lignins of the soda and sulfate pulping processes of Ricinus communis and bagasse was carried out by using successive equal concentrations of the alkaline reagent. Soda lignins were soluble in organic solvents, while the sulfate ones were sparingly soluble. Thus, two fractions of the sulfate lignins, soluble and insoluble, could be obtained from acetone. The different alkali lignin fractions were subjected to elemental and functional group analyses. For both Ricinus communis and bagasse, the carbon content of the fractions of the various types of lignin is in the order: soluble sulfate > soda > insoluble sulfate, while the methoxy is in the order: soda > soluble sulfate > insoluble sulfate. The phenolic OH content, as well as OH/C_9 of soda lignins of bagasse, are lower than those of soluble sulfate lignins. For Ricinus communis, the phenolic OH content and OH/C_9 is higher for some of the fractions (first three stages of cooking) of soda lignin than the corresponding fractions of kraft (sulfate) lignin, while the reverse takes place for the other fractions. For the same type of lignin, the fractions showed changes in their carbon, methoxyl, and phenolic OH contents. The change may be regular, i.e., increase or decrease with the order of stage of cooking, or

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irregular. Molecular weights of the different alkali lignins which are soluble in organic solvents ranged between 750 and 840.

INTRODUCTION

Most plant tissues contain an amorphous polymeric material called lignin in addition to carbohydrates and extractives. Plant lignin is concentrated mainly in the space between the cells (middle lamella) where it is deposited during the lignification of the plant tissues.

Lignin differs from the other two classes of natural polymers, carbohydrates and protein, by its aromaticity and insolubility in known solvents. It is also not hydrolyzable to monomeric units and is devoid of the highly regular structure. Electronic spcetroscopy indicates its aromaticity since it shows a band at 280 nm [1]. Infrared spectroscopy also shows an absorption band at 1600-1500 cm^{-1} due to the aromatic double bond stretching [2].

Plant lignins can be divided into three broad classes: softwood (gymnospers), hardwood (angiosperms), and grass lignins.

It has been suggested by Forss [3] that lignin is an ordered polymer composed of identical repeating units and is a three-dimensional network which obviously is bound to carbohydrates. Mansour et al. [4] found that alkali lignins isolated under mild conditions from cotton stalks and bagasse are actually low-molecular weight aromatic compounds. The conditions used to isolate such lignins were not enough to produce pulp from cotton stalks, while sufficient for pulping bagasse.

The aim of this work is to follow the structural changes of alkali lignins isolated through alkaline pulping processes from Recinus communis (representing woody plants) and bagasse (representing nonwoody plants). The alkali concentration was used to produce pulp from both plants. The isolated lignin from each was subjected to elemental and functional group analysis. The molecular weight of each lignin was determined by the Rast method [5].

EXPERIMENTAL

The aim of the pulping process is to remove noncellulosic materials. In the alkaline method a reaction takes place between sodium hydroxide and the enolic hydroxyl or phenolic groups in the lignin molecule to form a sodium compound which dissolves in dilute sodium hydroxide solution. In the case of the sulfate pulping process, the sodium sulfide used replaces some of the sodium hydroxide in the liquor, thus reducing the alkalinity and consequently having a less dependable effect. The conditions used for pulping are 20% sodium hydroxide based on raw material (oven dry) at a liquor ratio of 5:1. The maximum temperature was 160°C for 1 h. The sulfate method is carried out under the same con-

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ditions using 20% sulfidity, i.e., 20% sodium sulfide based on total alkali. The alkali was totally added in one case (one stage) and in another case was divided in portions of 5% total alkali concentration (multistage).

Isolation of Lignin from Black Liquor

At the end of the pulping time, the contents of the autoclave were filtered through a G_3 sintered glass funnel. The black liquor was acidified and then heated to 90°C on a water bath for 1 h in order to hydrolyze the carbohydrates. The isolated crude alkali lignin was then redissolved in sodium hydroxide solution. The concentrated hydrochloric acid was added dropwise until pH 3 was reached and the precipitate was filtered through a G_3 sintered glass funnel. The filtrate containing the alkali lignin was thoroughly cooled and then added to concentrated hydrochloric acid. Lignin was precipitated again in a nonfilterable form. The mixture was then heated gradually on a waterbath until the lignin coagulated into a filterable form. It was then filtered through filter paper, washed with 1% hydrochloric acid, and then washed with distilled water until neutrality was reached. Purification of lignin by the same method was carried out. The pure alkali lignin was dried in a vacuum oven at 40°C for 6 h. The dry product (brown in color) was a fine material containing less than 1% ash. The samples were preserved for further investigations.

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Analysis of Lignin

Elemental Analyses

Carbon and hydrogen were determined by the flash combustion technique. Nitrogen was determined by the micro-Dumas method [6]. Sulfur was determined by the Firtz and Yamamura method [7]. Oxygen was determined by difference. The analyses were carried out in the Microanalytical Laboratory, National Research Centre.

Chemical Analysis

Ash Content. This was carried out in a muffle furnace at 400°C for 1/2 h, then at 800°C for 3/4 h.

$$\text{ash content} = \frac{\text{weight of ash}}{\text{weight of sample (oven dry)}} \times 100$$

Methoxy Content. The methoxy group was determined by a modified version of the Zersel Viebecla method [8].

Phenolic OH by Electronic Spectra. This method is based on the characteristic ultraviolet absorption of phenols in alkaline solution [9, 10]. The absorption of an alkaline solution of the sample is measured directly against that of a neutralized portion of the same solution. The phenolic hydroxyl content of the sample is calculated from the maximum absorption of the resulting difference curve and the molar absorption maximum of model phenols determined in the same manner. In this work, phenolic OH has been estimated using the absorption at 250 nm as described by Wexler [9] rather than the absorbances at 300 nm as described by Goldschmid [10] because the latter method is limited to the determination of phenolic OH groups which are not conjugated with the C=O groups. On the other hand, the 250 nm maximum is common for both conjugated and nonconjugated phenolic compounds.

RESULTS AND DISCUSSION

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The results of elemental and functional group analysis are shown in Tables 1 and 2. From these tables the carbon content of the lignin fractions isolated from the black liquors of soda cooking is somewhat lower than those of the soluble lignin fractions isolated from kraft cooking for both bagasse and Ricinus communis. The insoluble kraft lignin fractions possess the lowest carbon content. The carbon content of the various types of lignin may therefore be in the order: soluble kraft lignin > soda lignin > insoluble kraft.

For the different types of lignin, i.e., soda and soluble and insoluble kraft of bagasse, the carbon content of the various lignin fractions decreases with the order of the cooking stage, i.e., for the 1st to the 4th stage (Table 1). For Ricinus communis, the change of the carbon content is irregular (Table 2).

The methoxy content MeO and the number of methoxyl group/C_9 for lignins isolated from black liquors of soda cooks are higher than those of kraft cooks, and both soluble and insoluble fractions for both bagasse and Ricinus communis (Tables 1 and 2). It appears that more than one methoxyl group relates to one phenyl propane unit for soda lignins. The methoxy content of the insoluble kraft lignins of both bagasse and Ricinus communis are too low, having a value of about 0.6 methoxyl group per phenyl propane unit on the average (Tables 1 and 2). The methoxy may be in the order: soda lignin > soluble kraft lignin > insoluble kraft lignin.

For the different types of lignin, the change of the methoxy content and the number of methoxyl group/C_9 of the various lignin fractions is irregular for both bagasse and Ricinus communis.

The phenolic OH content, estimated from the electron spectra (Fig. 1), as well as OH/C_9 of soda lignins of bagasse, are lower than those of soluble kraft lignins (Table 1). For Ricinus communis, the phenolic OH content and OH/C_9 for the first three stages (1, 2, 3) of soda lignin is higher than the correspondings of kraft lignin, while the reverse holds

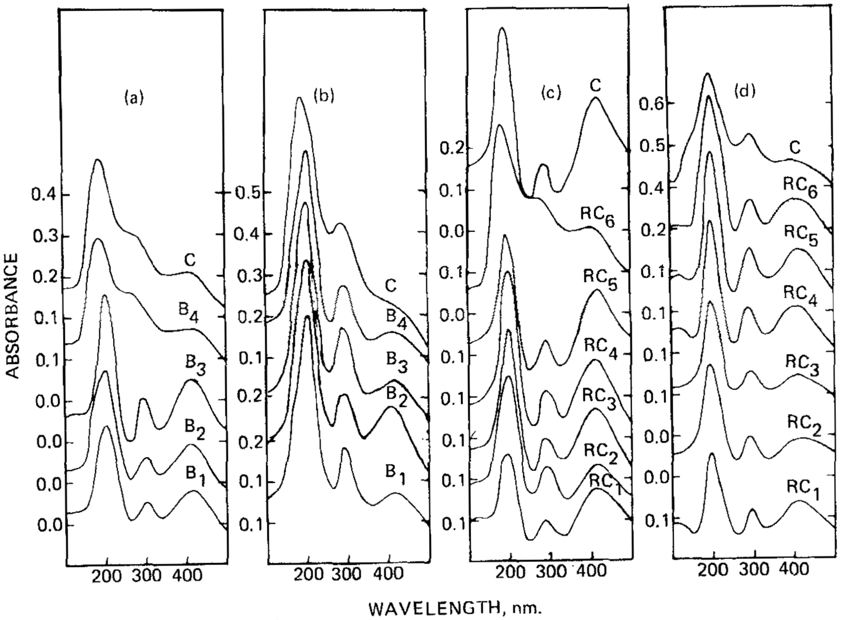

FIG. 1. UV difference spectra for various lignin spectra. (a) Lignins from soda-cooked bagasse. (b) Soluble lignins from kraft-cooked bagasse. (c) Lignins from soda-cooked Ricinus communis. (d) Lignin from kraft-cooked Ricinus communis. The subscripts indicate the cooking stage, and the top curves (C) indicate a one-step complete cook.

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true for the other stages (4, 5, 6) (Table 2). For soda cooking of bagasse (Table 1), the phenolic OH content and OH/C_9 increased with an increase in the order of the cooking stage, i.e., from stage 1 to 4, while kraft cooking showed an irregular change. On the other hand, for soda cooking of Ricinus communis (Table 2), there is either no change or an increase of phenolic OH with an increase of the order of the cooking stage, while for kraft cooking (soluble kraft lignin) there is a steady increase with the order of cooking stage.

The ratio of OH/OCH_3 for soluble lignins of the kraft cook of bagasse is significantly higher than the lignins of the soda cook, while for Ricinus communis the change of OH/OCH_3 is insignificant (Table 3). This may reveal the dependence of the ratio OH/OCH_3 on the method of cooking.

Molecular weights determined by the Rast method [5] are listed in Tables 1 and 2. It is seen that the molecular weights of all lignins isolated from the black liquors of the kraft and soda processes varied between 750 and 840. The average molecular weight is 796 with a

TABLE 1. Results of Chemical Analyses and Functional Groups in

Sample	Cooking Stage	% of atoms and functional groups C	H	S	O	OH	OCH_3
Lignin from soda cook	1	62.6	5.6	-	31.8	1.2	15.8
	2	62.1	6.0	-	31.9	1.3	17.0
	3	61.9	6.0	-	32.1	1.7	16.6
	4	61.7	5.9	-	32.4	1.9	16.0
	C[a]	61.8	6.0	-	32.3	2.3	16.6
Soluble lignin from kraft cook	1	64.6	5.7	4.0	25.7	2.9	13.5
	2	64.2	5.7	4.2	25.9	3.3	13.7
	3	63.6	5.8	4.4	26.2	3.0	14.5
	4	63.5	5.9	4.9	25.7	3.3	13.5
	C[a]	63.8	5.7	4.4	26.2	3.5	14.4
Insoluble lignin from kraft cook	1	60.0	6.2	3.4	30.9	-	11.5
	2	59.5	6.1	4.5	30.0	-	10.5
	3	59.2	6.0	5.0	30.0	-	10.3
	4	59.1	6.0	5.5	29.4	-	10.1
	C[a]	59.2	6.0	5.3	29.5	-	10.2

[a] Denotes the one-step full cooking process.

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Lignins from Multistage Soda and Kraft Cooking of Bagasse

Number of atoms and functional groups						Structural weight	Molecular weight
C	H	S	O	OH	OCH_3		
9	7.7	-	2.7	0.13	0.97	191	780
9	8.4	-	2.8	0.15	1.1	195	820
9	8.4	-	2.7	0.20	1.0	195	800
9	8.2	-	2.7	0.22	1.0	195	790
9	8.2	-	2.6	0.26	1.0	195	795
9	7.7	0.23	1.8	0.31	0.79	182	790
9	7.7	0.24	1.8	0.36	0.81	183	810
9	7.9	0.26	1.9	0.33	0.87	186	900
9	8.1	0.28	1.8	0.36	0.80	185	800
9	7.6	0.25	1.8	0.38	0.86	186	840
9	10.0	0.21	3.1	-	0.73	196	-
9	9.9	0.28	3.0	-	0.66	195	-
9	9.9	0.31	3.0	-	0.65	196	-
9	9.8	0.34	3.0	-	0.64	196	-
9	9.9	0.32	3.0	-	0.65	196	-

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TABLE 2. Results of Chemical Analyses and Functional Groups in

	Cooking	% of atoms and functional groups					
Sample	Stage	C	H	S	O	OH	OCH_3
Lignin from soda cook	1	60.0	6.0	-	34.1	1.3	17.8
	2	62.2	6.0	-	33.8	1.7	17.5
	3	60.9	6.0	-	33.1	1.7	16.9
	4	61.0	5.9	-	33.1	1.7	16.5
	5	61.2	5.8	-	33.0	1.9	16.2
	6	61.2	5.8	-	33.0	2.2	16.3
	C[a]	60.3	6.0	-	33.8	2.3	17.4
Soluble lignin from kraft cook	1	63.2	5.9	3.9	27.1	1.2	14.9
	2	63.4	6.0	3.9	26.7	1.3	15.5
	3	63.6	6.0	4.2	26.1	1.6	15.3
	4	63.8	6.1	4.5	25.7	2.0	15.4
	5	63.2	5.9	4.6	26.3	2.4	14.8
	6	63.1	5.9	4.6	26.4	2.6	14.4
	C[a]	63.2	6.0	4.5	26.3	3.3	15.0
Insoluble lignin from kraft cook	1	57.3	5.6	4.0	33.1	-	10.2
	2	57.6	5.4	4.2	32.8	-	10.5
	3	58.0	5.4	4.4	32.2	-	11.3
	4	58.0	5.4	4.5	32.0	-	11.2
	5	58.0	5.3	4.6	32.1	-	11.1
	6	58.5	5.3	5.3	30.9	-	10.5
	C[a]	58.1	5.3	4.6	30.0	-	9.5

[a] Denotes the one-step full cooking process.

Lignins from Multistage Soda and Kraft Cooking of Ricinus Communis

Number of atoms and functional groups						Structural weight	Molecular weight
C	H	S	O	OH	OCH_3		
9	8.4	-	3.0	0.16	1.2	203	800
9	8.5	-	2.9	0.21	1.1	202	790
9	8.5	-	2.8	0.21	1.1	198	780
9	8.3	-	2.8	0.20	1.1	198	770
9	8.0	-	2.8	0.22	1.0	197	750
9	8.0	-	2.8	0.25	1.0	197	760
9	8.3	-	2.9	0.27	1.1	202	790
9	8.2	0.23	2.1	0.14	0.9	188	800
9	8.2	0.23	2.1	0.14	0.9	188	810
9	8.4	0.25	2.0	0.18	0.9	187	790
9	8.4	0.26	1.9	0.22	0.9	187	800
9	8.1	0.27	1.9	0.26	0.9	188	780
9	8.2	0.27	1.9	0.27	0.9	188	760
9	8.2	0.27	1.9	0.36	0.9	188	800
9	9.4	0.25	3.5	-	1.7	202	-
9	8.9	0.27	3.5	-	0.7	202	-
9	8.9	0.28	3.3	-	0.7	201	-
9	8.7	0.28	3.3	-	0.7	201	-
9	8.5	0.29	3.3	-	0.7	201	-
9	8.5	0.33	3.2	-	0.7	198	-
9	8.0	0.28	3.4	-	0.6	198	-

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TABLE 3. Ratio of Functional Group/Phenolic OH to OCH_3 Group in Soda and Kraft Cooks of Bagasse and Ricinus communis

Sample	Cooking stage	OH/OCH_3	Sample	Cooking stage	OH/OCH_3
Lignins from soda cook of bagasse	1	0.134	Soluble lignins from kraft cooking of bagasse	1	0.388
	2	0.142		2	0.44
	3	0.192		3	0.379
	4	0.220		4	0.450
	C[a]	0.250		C[a]	0.443
Lignins from soda cook of Ricinus communis	1	0.133	Soluble lignins from kraft cooking of Ricinus communis	1	0.149
	2	0.180		2	0.153
	3	0.194		3	0.188
	4	0.190		4	0.237
	5	0.214		5	0.290
	6	0.241		6	0.308
	C[a]	0.240		C[a]	0.395

[a] Denotes the one-step full cooking process.

standard deviation of ± 30. This standard deviation amounts to only 15% of the structural unit weight, which indicates that the number of the structural units in the molecule is the same for various lignin preparations. The molecular formulas for all lignin preparations are as follows.

Soda Lignins

Bagasse:

1st stage	$C_{37}H_{32}O_{11}(OH)_{0.53}(OCH_3)_{4.0}$
2nd stage	$C_{38}H_{35}O_{11}(OH)_{0.63}(OCH_3)_{5.0}$
3rd stage	$C_{37}H_{34}O_{11}(OH)_{0.82}(OCH_3)_{4.0}$
4th stage	$C_{37}H_{33}O_{11}(OH)_{0.89}(OCH_3)_{4.0}$
One-stage	$C_{37}H_{34}O_{11}(OH)_{1.06}(OCH_3)_{4.0}$

Ricinus communis:

1st stage	$C_{35}H_{33}H_{12}(OH)_{0.61}(OCH_3)_{5.0}$
2nd stage	$C_{35}H_{33}O_{11}(OH)_{0.81}(OCH_3)_{4.0}$
3rd stage	$C_{35}H_{33}O_{11}(OH)_{0.81}(OCH_3)_{4.0}$
4th stage	$C_{35}H_{32}O_{11}(OH)_{0.78}(OCH_3)_{4.0}$
5th stage	$C_{34}H_{31}O_{11}(OH)_{0.84}(OCH_3)_{4.0}$
6th stage	$C_{34}H_{31}O_{11}(OH)_{0.97}(OCH_3)_{4.0}$
One-stage	$C_{34}H_{32}O_{11}(OH)_{1.06}(OCH_3)_{4.0}$

Kraft Lignins

Bagasse:

1st stage	$C_{39}H_{33}O_8(OH)_{1.33}(S)_{0.99}(OCH_3)_{3.0}$
2nd stage	$C_{40}H_{34}O_8(OH)_{1.58}(S)_{1.06}(OCH_3)_{4.0}$
3rd stage	$C_{44}H_{38}O_8(OH)_{0.60}(S)_{1.24}(OCH_3)_{4.0}$
4th stage	$C_{39}H_{35}O_9(OH)_{1.56}(S)_{1.21}(OCH_3)_{4.0}$
One-stage	$C_{41}H_{34}O_8(OH)_{1.73}(S)_{1.14}(OCH_3)_{4.0}$

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Ricinus communis:

1st stage	$C_{38}H_{35}O_9(OH)_{0.57}(S)_{0.97}(OCH_3)_{4.0}$
2nd stage	$C_{39}H_{35}O_9(OH)_{0.62}(S)_{0.99}(OCH_3)_{4.0}$
3rd stage	$C_{38}H_{35}O_8(OH)_{0.73}(S)_{1.0}(OCH_3)_{4.0}$
4th stage	$C_{39}H_{36}O_8(OH)_{0.94}(S)_{1.0}(OCH_3)_{4.0}$
5th stage	$C_{37}H_{34}O_8(OH)_{1.0}(S)_{1.0}(OCH_3)_{4.0}$
6th stage	$C_{36}H_{33}O_8(OH)_{1.0}(S)_{1.0}(OCH_3)_{4.0}$
One-stage	$C_{38}H_{33}O_8(OH)_{1.5}(S)_{1.13}(OCH_3)_{4.0}$

From these molecular formulas it is clear that the number of carbon atoms, as well as the number of oxygen atoms, is higher for the kraft lignins than those of soda lignin for both bagasse and Ricinus communis, taking into consideration that the kraft lignins are the acetone-soluble fractions.

The number of hydrogen atoms is the same for all lignins. For the kraft and soda lignins of bagasse, the number of carbon atoms is somewhat higher than those of Ricinus communis.

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